Statistical Thermodynamics in Chemistry and Biology

Introduction to electrostatics

Per-Olof Åstrand

D3-119 Realfagsbygget, Department of Chemistry,
Norwegian University of Science and Technology,
per-olof.aastrand@ntnu.no

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Introduction to electrostatics

- These notes are an alternative (as compared to the book) introduction to concepts like electrostatic potential, electric field and dipole moment.

Introduction to electrostatics

Part 2

- The interaction between two charges, q_i and q_j, are given by an empirical law, Coulomb's law, which is the starting point in electrostatics,

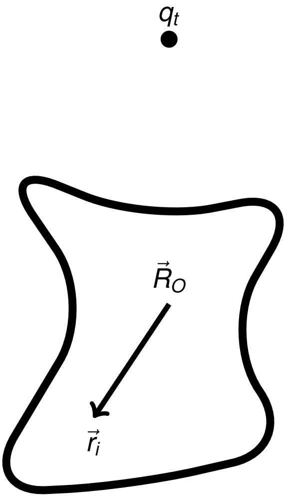
$$V(R) = \frac{q_i q_j}{4\pi\varepsilon_0 R}$$

where ε_0 is the permittivity of vacuum and R is the distance between the charges.

- Regard the interaction between a set of charges, $q_i, i = 1, \ldots, N$, (e.g. a molecule) and a test charge q_t. See figure.

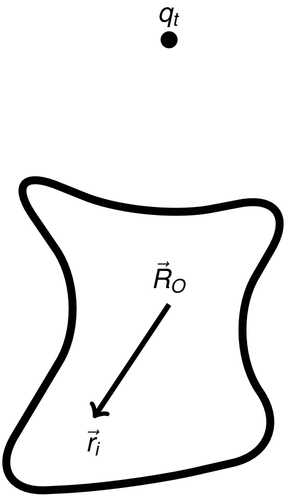
$$V = \sum_i^N \frac{q_i q_t}{4\pi\varepsilon_0 R_{it}}$$

where interactions within the molecule has been ignored.



Electrostatic potential

- Define the electrostatic potential, ψ_i, at charge i, as
$$V = \sum_i^N \frac{q_i q_t}{4\pi\varepsilon_0 R_{it}} = \sum_i^N q_i \psi_i$$
so that
$$\psi_i = \frac{q_t}{4\pi\varepsilon_0 R_{it}}$$
- We note that the electrostatic potential is additive, since we can also write
$$V = q_t \psi_t$$
since
$$\psi_t = \sum_i^N \frac{q_i}{4\pi\varepsilon_0 R_{it}}$$

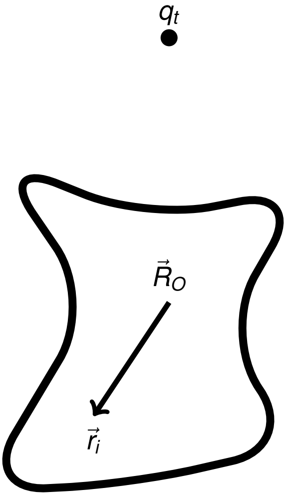


Multipole expansion

- The next step is to carry out a multipole expansion, i.e. a Taylor expansion of the electrostatic potential, ψ_i, around the origin of the molecule, $\vec{R}_O$. In one dimension, x, it becomes,

$$\psi_i = \psi_O + r_{i,x}\frac{\partial \psi_O}{\partial x} + \cdots$$

where ψ_O is the electrostatic potential calculated at the origin and $\frac{\partial \psi_O}{\partial x}$ is its gradient, also calculated at the origin.



Multipole expansion

Part 2

- Putting the multipole expansion into the expression for the energy,

$$V = \sum_i^N q_i \psi_i = \sum_i^N q_i \psi_O + q_i r_{i,x} \frac{\partial \psi_O}{\partial x} + \dots$$

$$= \left(\sum_i^N q_i \right) \psi_O + \left(\sum_i^N q_i r_{i,x} \right) \frac{\partial \psi_O}{\partial x} + \dots$$

- Define the molecular charge, q^{mol}, as

$$q^{\mathrm{mol}} = \sum_i^N q_i$$

- the molecular dipole moment, $\vec{\mu}^{\mathrm{mol}}$, as

$$\vec{\mu}^{\mathrm{mol}} = \sum_i^N q_i \vec{r}_i$$

Multipole expansion

Part 3

- the electric field, $\vec{E}_O$ calculated at the origin O as

$$\vec{E}_O = -\vec{\nabla}\psi_O \; ; \quad \text{In one dim.:} E_{x,O} = -\frac{\partial \psi_O}{\partial x}$$

- The end result for the energy becomes,

$$V = q^{\mathrm{mol}}\psi_O - \vec{\mu}^{\mathrm{mol}} \cdot \vec{E}_O + \cdots$$

  i.e. the interaction can be obtained from molecular multipole moments (charge, dipole moment, etc.) and the electrostatic potential, electric field, etc. calculated at the origin of the molecule.

- This energy term can be added to the internal energy, U, and can thus be included the thermodynamics machinery.

Summary

- An introduction to electrostatics starting at Coulomb's law.
- Define electrostatic potential.
- A multipole expansion gives concepts like the electric field and dipole moment.
- Energy expression to used in statistical thermodynamics (to be added to dU).
- Trivial to extend to charge-dipole and dipole-dipole interactions, quadrupole moments, etc.